TABLE XI

THE ENTROPY OF HEXAFLUOROETHANE IN THE IDEAL GAS STATE AT CERTAIN TEMPERATURES FROM MOLECULAR AND SPECTROSCOPIC DATA

T, °K.	176.61	194.87
V, cal. per mole	4350	4350
$S_{t,r}$	60.79	61.58
S_f, one degree of freedom	5.73	5.83
S_v	3.97	4.82
$-(S_f - S)$	−2.52	−2.41
Total	67.97	69.82
Calorimetric	67.92	69.88

A potential barrier of 4350 calories per mole restricting the free rotation of the CF_3 group in hexafluoroethane gives the best fit between the theoretical and experimental entropy of the gas.

That a barrier exists is indicated by the appearance of only seven lines in the Raman spectrum. If rotation were free, the activity of the fundamental frequencies of species E_u, when added to that of A_{1g} and E_g which are already active in the Raman spectrum, should result in more lines in the Raman spectrum.

Heat capacity data on the gas would be helpful in confirming the value for the height of the barrier. Its present value indicates that potential barriers are not due to peculiar properties of hydrogen atoms.

Acknowledgments.—We wish to thank Dr. J. H. Simons of the Fluorine Laboratory for the calorimetric sample of high purity. We are indebted to Dr. D. H. Rank of the Spectroscopy Laboratory for the Raman Spectrum and to Dr. J. Rud Nielsen of the University of Oklahoma Research Institute for the infrared spectrum and the aid in its interpretation. The work was made possible by the financial aid provided by the Phillips Petroleum Fellowship.

Summary

1. The heat capacity of hexafluoroethane has been measured from 11.2 to 195.0° K. as well as the density of the gas at 298.16° K.

2. The molal heat of transition of hexafluoroethane has been measured and the average transition temperature determined.

3. The molal heat of fusion together with the solid–liquid–vapor equilibrium temperature of the pure compound has been determined.

4. The vapor pressures of the solid and the liquid to the normal boiling point have been measured.

5. The molal heat of vaporization of hexafluoroethane has been determined for the liquid as a function of the temperature as well as the volumes of the saturated vapor.

6. From the experimental data, the entropy of the gas has been computed at the normal boiling point and at a temperature at which the vapor pressure of the liquid is one-third of an atmosphere.

7. The entropy of the gas has been calculated from a frequency assignment based on the infrared spectrum of the gas and a Raman spectrum of the liquid. A potential barrier of 4350 calories per mole hindering the mutual rotation of the CF_3 groups gives the best agreement between the calculated and the calorimetric entropy.

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[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1]]

Equilibrium Moisture and X-Ray Diffraction Investigations of Pectinic and Pectic Acids

BY K. J. PALMER, R. C. MERRILL AND M. BALLANTYNE

In order to obtain some insight into the influence of polar groups on the sorption[2] of water by hydrophilic polymers, the equilibrium moisture contents have been determined for a series of pectinic and pectic acids[3] which have methyl ester contents between 0.2 and 10.9%. This range in methyl ester content corresponds to a variation in free carboxyl groups in the polygalacturonic acid part of the sample of about 23 to 99% when the nonuronide content is taken into account. This series of samples, therefore, offers the opportunity of determining the influence of free and esterified carboxyl groups on the equilibrium moisture content at various relative humidities. There was also the possibility that the data could be used to deduce the amount of water associated with the free and esterified carboxyl groups. Unfortunately, this latter possibility is not realized because, as it turned out, the equilibrium moisture content was essentially independent of the degree of esterification.

It is now quite evident that in addition to the polar groups, the packing of the chains in the crystalline regions plays an important role in determining the equilibrium moisture content of many hydrophilic polymers. For this reason, X-ray diffraction photographs of powders of each sample

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[2] The term sorption is used in this paper to indicate the uptake of water; desorption the reverse of this process.

[3] The terms pectinic and pectic acid are used in this paper in accordance with the recommendation of the Committee for Revision of the Nomenclature of Pectic Substances. *Chem. Eng. News*, April 25, 609 (1944).

equilibrated at various relative humidities between zero and 95% were taken. The results of this investigation are reported in this paper.

Experimental

The pectinic and pectic acids were prepared and purified by previously published methods.[4a,b] Table I lists some of the significant analytical data for these compounds. Column one of Table I gives the number of the sample, while column two of Table I gives the methyl ester content as well as the method of de-esterification. The letters A, B and E used in column two of Table I refer to acid,[5] alkaline,[6] and enzymatic[7] de-esterification, respectively. The samples were de-ashed either with ion-exchange resins[4a] or by precipitation in acid alcohol. The ash content of each sample is shown in column three of Table I. The uronic acid content, expressed as uronic acid anhydride, is given in column four of Table I, while column five of this table gives the value of the intrinsic viscosity.

TABLE I

ANALYTICAL DATA FOR THE PECTINIC AND PECTIC ACID SAMPLES USED IN THIS INVESTIGATION

Sample	MeO.[a] %	Ash. %	Uronic acid anhydride. %	Intrinsic viscosity. (η)	De-esterification. %
L51	10.9	0.4	(80)	9.3	(23)
804	8.0 A	1.18	82	4.2	44
L64	7.4 E	0.4	79	5.5	47
L37P	5.8 E	0.4	82	4.8	59
L81	4.5 E	0.5	80	5.2	68
805	3.0 A	1.53	89	2.8	81
L67	2.7 E	0.29	81	3.5	81
619	0.4 B	0.6	86	2.7	97.4
L69	0.2 E	0.2	82	3.7	98.6

[a] The letters A, B and E signify acid, base and enzyme de-esterification, respectively.

Before samples were equilibrated at various relative humidities, they were humidified for forty-eight hours by placing them in a desiccator containing water. Alcohol sorbed as a result of the method of preparation is presumably removed by this procedure.[8] The desorption equilibrium moisture content was obtained in the following manner.[9] Two-hundred milligrams of each humidified sample were put in a small weighing bottle having a ground-glass top. Duplicate bottles of each sample, with tops on edge, were placed in a series of ten vacuum desiccators having relative humidities of 2, 6, 15, 24, 36, 49, 58, 84, 88, and 95%. The relative humidities in the desiccators were controlled by using sulfuric acid solutions of suitable concentrations. The desiccators were then evacuated and allowed to stand in a constant-temperature room held at 25 ± 1° for a period of two weeks. Thereafter the samples were weighed every week. In all cases at the end of five weeks the weights had not varied by more than 0.3 mg. from the weighings of the previous week, except for the samples at 95% relative humidity. In the latter case the weighings fluctuated in general by about 3 mg. This fluctuation was probably due to inadequate temperature control (±1°). At all relative humidities except 95%, equilibrium was assumed to have been reached when the samples maintained constant weight to within 0.3 mg. over a period of one week. At 95% relative humidity, the samples were assumed to be at equilibrium at the end of the five-week period.

The moisture content was determined by heating the samples in a vacuum oven at 70° for sixteen hours and noting the loss in weight. This leads to an essentially constant dry weight, although like the proteins,[10] further heating results in a measurable, though very slight, loss in weight.[11] The percentage loss in weight of the duplicate samples agreed in all cases (except at 95% relative humidity) to within 0.2%. The equilibrium sorption water contents were obtained by placing the vacuum oven-dried samples back into the various constant relative humidity desiccators and determining the gain in weight. The same weighing procedure was followed as described above for desorption.

X-Ray powder photographs were taken by placing some of the equilibrated material in thin-walled soft glass capillaries. The filled capillaries were allowed to stand with one end open in the appropriate sulfuric acid desiccator for an additional week. Upon removal from the desiccators the open end of each of the capillaries was quickly sealed by a small flame. Copper radiation filtered through a thin nickel foil was used.

Results

The equilibrium moisture contents of the various samples investigated, expressed in per cent. of dry weight, are given in Table II. The first column of Table II lists the number of the sample. In the next ten columns the equilibrium moisture contents at 25° are given for the relative humidities shown at the top of the columns. The last column indicates whether equilibrium was attained by desorption or sorption. At relative humidities of 84% and above, the sorption and desorption values were found to be the same within experimental error; therefore, only one value is listed. The moisture contents given for 95% relative humidity are not as accurate as those for the other relative humidities because of the difficulty experienced in reaching what could be reliably taken as a constant weight during equilibration.

Figure 1 shows a plot of the equilibrium moisture content *versus* relative humidity for both sorption and desorption for pectinic acid L81. The moisture isotherm curves are so similar for all the samples investigated that only those for L81 are shown.

The X-ray patterns of pectinic and pectic acids show in general three characteristic reflections,[12] although under certain conditions, such as high water content or heat degradation, several additional reflections appear. A typical X-ray diffraction photograph of a high-molecular weight pectinic acid is shown in Fig. 2. The inner rather diffuse ring is the only one which shows an appreciable variation with water content. Plots of this spacing against moisture content are shown in

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(4) (a) H. S. Owens, H. Lotzkar, R. C. Merrill and M. Peterson, THIS JOURNAL, **66**, 1178 (1944); (b) T. H. Schultz, H. Lotzkar, H. S. Owens and W. D. Maclay, *J. Phys. Chem.*, **49**, 554 (1945).

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(9) B. Makower and D. L. Dehority, *ibid.*, **35**, 193 (1943).

(10) H. B. Bull, THIS JOURNAL, **66**, 1499 (1944).

(11) C. M. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 312 (1945).

(12) K. Wuhrmann and W. Pilnik, *Experimentia*, **1**, 330 (1945). K. J. Palmer, R. C. Merrill, H. S. Owens and M. Ballantyne, *J. Phys. and Colloid Chem.*, **51**, 710 (1947).

TABLE II

MOISTURE CONTENTS AT 25° IN PER CENT. OF DRY WEIGHT AT THE RELATIVE HUMIDITIES SHOWN AT THE TOP OF THE COLUMN

Sample	2%	6%	15%	24%	36%	49%	58%	84%	88%	95%	Remark
L51	2.5	...	8.3	11.1	14.2	17.4	19.6	26.4	34.5	57	Desorption
	...	4.5	7.7	9.7	11.7	15.8	17.4				Sorption
804	2.6	5.4	...	11.5	..	18.3	20.6	28.7	36.3	44.7	Desorption
L64	2.8	...	9.4	11.8	15.1	18.6	20.3	28.0	36.8	53	Desorption
	...	4.2	7.0	9.1	12.4	16.6	18.6				Sorption
L37P	...	...	8.9	11.3	14.3	17.7	20.0	27.8	37.3	63	Desorption
	...	3.2	7.6	8.9	11.2	16.0	18.1				Sorption
L81	2.8	5.6	9.1	11.6	14.7	18.2	20.5	29	..	52.5	Desorption
	2.0	4.2	6.6	9.0	12.4	16.3	19.1				Sorption
805	2.9	6.0	...	11.8	..	18.1	20.1	29.3	36.6	46.2	Desorption
L67	3.2	5.2	9.4	12.0	15.1	18.4	21.0	30.1	38.7	56	Desorption
	...	...	8.7	10.7	13.1	15.8	19.1				Sorption
619	2.6	5.2	...	10.7	..	17.0	18.9	..	34.4	43.3	Desorption
L69	2.8	5.8	9.1	11.7	14.6	18.3	20.4	28.7	36.9	51	Desorption
	2.0	4.3	6.4	8.9	12.2	15.5	18.5				Sorption

Figs. 3, 4 and 5 for the various samples investigated.

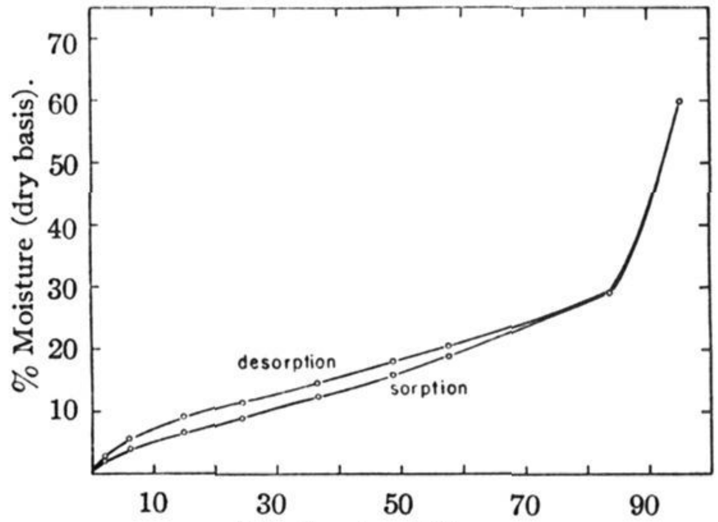

Fig. 1.—Sorption and desorption moisture isotherms for pectinic acid L81 at 25°.

Discussion

Equilibrium Moisture Content.—As shown in Table II, one of the results which is immediately evident from this investigation is that the equilibrium moisture content is essentially independent of methyl ester content over the whole relative humidity range with the possible exception of the results obtained at the highest relative humidities. This is rather surprising in view of the fact that the methyl ester content varies between 10.9 and 0.2%. This represents a change from about one free carboxyl per four galacturonide units to one free carboxyl for each galacturonide unit.

The constancy of the equilibrium water content with variation in free carboxyl groups is illustrated in Fig. 6. In this figure the water sorbed is plotted against the per cent. of free carboxyl groups. The latter value was determined from the uronic anhydride values listed in Table I. For example, sample L64 has a methyl ester content of 7.4% and a uronic anhydride value of 79%. This corresponds to 7.4(100/79) = 9.36% methyl ester on the basis of the galacturonide content. On the same basis completely esterified pure polygalacturonic acid would have a methyl ester content of 17.6%; therefore, 46.6% of the carboxyl groups in L64 are not esterified. The results of similar calculations on the other samples are shown in column six of Table I.

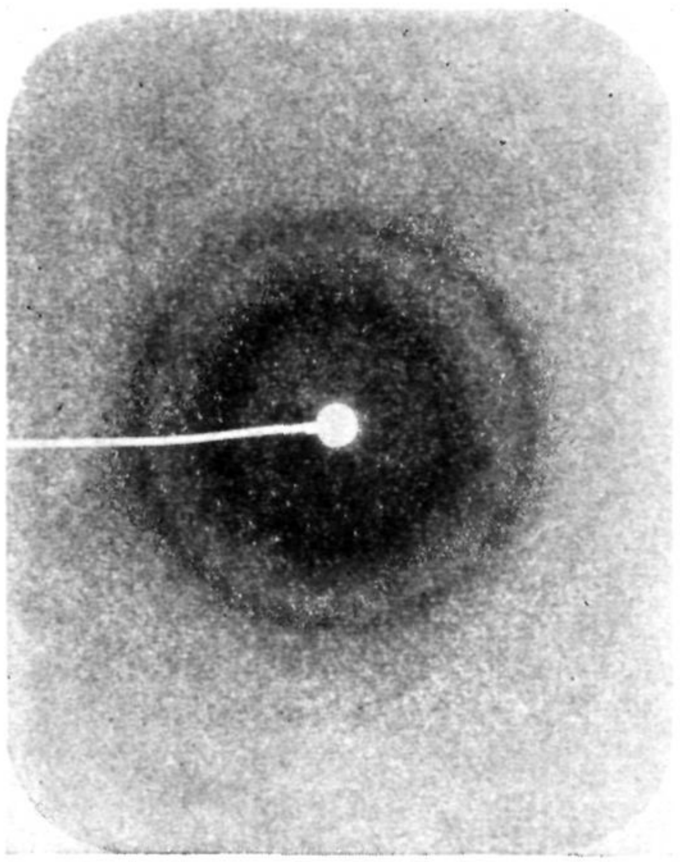

Fig. 2.—X-Ray diffraction photograph of pectinic acid L64, equilibrated at 36% relative humidity. CuKα, Ni filter, camera distance 5.0 cm.

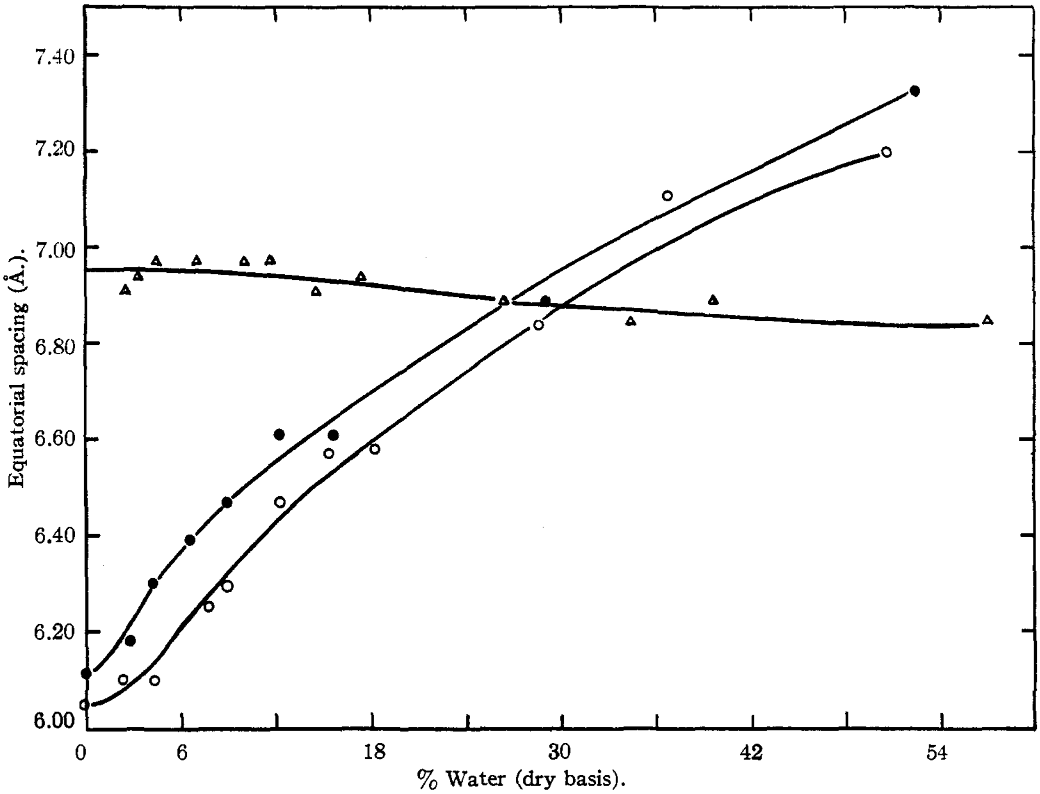

Fig. 3.—Variation of the interplanar spacing calculated from the equatorially accentuated X-ray reflection plotted against moisture content for pectinic acids L51, L81 and for pectic acid L69. Samples equilibrated by sorption: ○ L69, 0.2% MeO; ● L81, 4.5% MeO; △ L51, 10.9% MeO.

The fact that all of the curves in Fig. 6 are essentially horizontal indicates that the number of free carboxyl groups does not affect the equilibrium moisture content of the pectinic acids in the relative humidity range of 2 to 88% at 25°. Results of an equilibrium moisture content study on several proteins[13] indicate that the carboxyl groups in these materials also do not play a major role in determining the water sorption capacity of proteins. On the other hand, a recent study of the equilibrium moisture content of casein and several derivatives in which the amino groups have been benzoylated[14] show that the amino group markedly affects water sorption.

The results obtained in the case of the pectinic acids can be interpreted in several ways. The most obvious is to assume that the hydroxyl groups are primarily responsible for the high water sorption of the pectinic acids. This assumption receives some substantiation from the fact that the equilibrium water content is markedly reduced when the hydroxyl groups are esterified with proprionic acid[15] in contrast to the negligible effect observed when the carboxyl groups are esterified.

On the other hand, the comparatively low water sorption of cellulose and the fact that carboxyl groups usually show a greater affinity for water than hydroxyl groups[16] indicate that the mechanism of water sorption by long-chain polymers involves factors other than the hydration affinity of the polar groups.

One important factor is the availability of the polar groups in the crystalline regions. The fact that water does not penetrate the crystallites in native cellulose, for example, in spite of the numerous polar groups, is well established.[17] The ability of the crystallites in native cellulose, silk and presumably nylon[18] to resist penetration by water is probably due to the fact that the polymer chains can pack well together, because in these substances there are no bulky side chains. The close packing of the chains allows a large number of secondary interchain bonds to be established which, acting together, give rise to a comparatively stable structure.

A second, though closely related, way for a polar

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(13) H. Fraenkel-Conrat and H. S. Olcott, *J. Biol. Chem.*, **161**, 259 (1945); H. S. Olcott and H. Fraenkel-Conrat, *Ind. Eng. Chem.*, **38**, 104 (1946).

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(15) The sorption equilibrium water content of pectin propionate when in equilibrium with an atmosphere having a relative humdity of 60% is only 2.1%.

(16) O. L. Sponsler, J. D. Bath and J. W. Ellis, *J. Phys. Chem.*, **44**, 996 (1940).

(17) P. H. Hermans and A. Weidinger, *J. Colloid Science*, **1**, 185 (1946). See also P. H. Hermans, "Contribution to the Physics of Cellulose," Elsevier Publishing Co., New York, N. Y., 1946, p. 50.

(18) M. Dole and A. D. McLaren, THIS JOURNAL, **69**, 651 (1947).

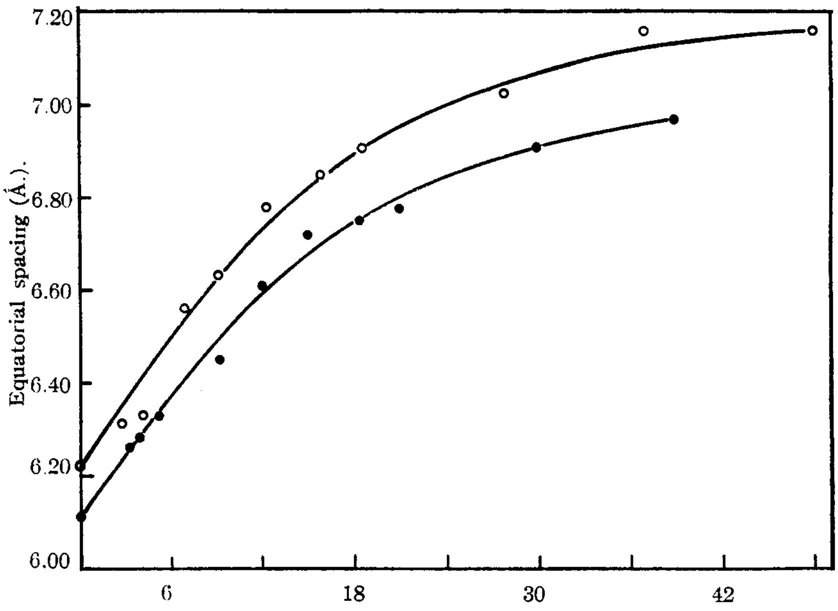

Fig. 4.—Variation of the interplanar spacing calculated from the equatorially accentuated X-ray reflection plotted against moisture content for pectinic acids L64 and L67. Samples equilibrated by sorption: ●, L67, 2.75% MeO; ○, L64, 7.4% MeO.

group to show an unexpectedly low affinity for water is by formation of an interchain bond with another polar group of sufficient strength to resist the dissociating effect of water even though water penetrates between the chains in the crystallites. The pectinic and pectic acids appear to behave in this way. The greater hygroscopicity of the free carboxyl group over the esterified one is probably compensated for in the pectinic acids by the relatively strong interchain hydrogen bonds formed between two adjacent carboxyl groups. The existence of stronger interchain bonds in pectic acid as compared to high methyl ester pectinic acids is substantiated by the fact that pectic acid is not soluble in water at its natural *p*H, whereas the high methyl ester pectinic acids readily go into solution.

Another example of the importance of the availability of the polar groups as sorbing sites in determining the equilibrium moisture content is illustrated by the results found for sodium pectate.[19] The crystallites in sodium pectate sorb a maximum of about 24% water at a relative humidity of 95% at 25°, although the water content of the sample is 64%. The probable reason for this discrepancy is evident from the X-ray photographs. At low moisture contents the X-ray photographs show poor crystallinity; consequently, water readily penetrates between the chains and hydrates the polar groups. When the water content in the crystallites approaches 20% the sodium pectate chains begin to assume a crystalline arrangement. The increase in crystallinity during sorption is apparent from the X-ray photographs.[19] After the hydrated sodium pectate chains have crystallized, the interchain forces (probably involving water bridges) are evidently sufficiently strong to resist further penetration by water molecules. As a consequence the polar groups in the crystallites of sodium pectate are not available for further sorption at relative humidities above about 40% at 25°.

Hysteresis.—In all cases where both desorption and sorption moisture data have been obtained on the pectinic and pectic acids it is evident that a definite hysteresis occurs. Whether the hysteresis is real or due to a very slow approach to equilibrium cannot be stated with certainty, since the definition of equilibrium has been arbitrarily taken as the attainment of a constant weight for one week. The observed hysteresis is reversible in the sense that a sample can be repeatedly taken around the hysteresis loop.

In the two samples L81 and L69 investigated at low relative humidities, the hysteresis appears to persist down to the lowest relative humidities investigated. This has also been observed in many other cases where water sorption is accompanied by swelling,[20] but is not observed, in general, in those cases where the sorbate does not cause swelling.[21] The extension of the hysteresis to essentially zero relative humidity is probably a manifestation of the fact that when swelling occurs the last traces of water to be removed are internally bound, *i.e.*, inside the crystallites, whereas the first water taken up is sorbed in the amorphous regions and on the surface of the crystallites.

This hypothesis is supported by the results obtained on sodium pectate.[19] In this case the X-ray spacings can be more reliably measured than in the case of the pectinic acids and the results show that the interchain separation in the crystallites continues to decrease down to zero moisture content, but on sorption there is a definite lag in the uptake of water by the crystallites. In other words, the crystallites also exhibit a hysteresis which appears to extend to zero moisture content. A similar effect probably occurs in the pectinic acids, although it may be less pronounced and in

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(20) J. B. Speakman, *J. Textile Inst.*, **27**, T185 (1936).

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any case is more difficult to demonstrate because the X-ray reflection is too diffuse to measure accurately.

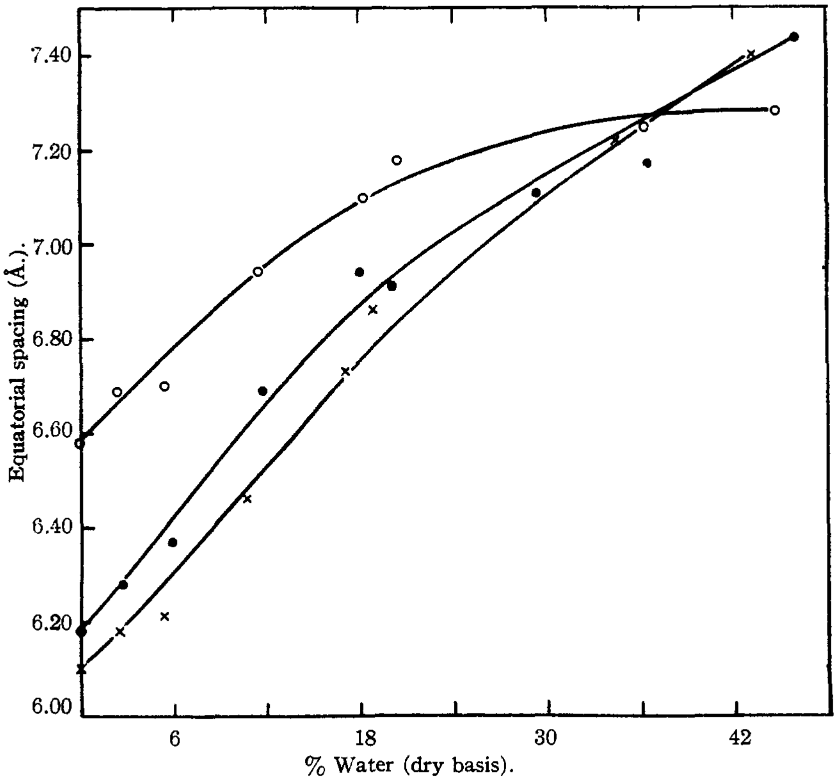

Fig. 5.—Variation of the interplanar spacing calculated from the equatorially accentuated X-ray reflection plotted against moisture content for pectinic acids 804 and 805 and pectic acid 619. Samples equilibrated by desorption: ×, 619, 0.4% MeO; ●, 805, 3.0% MeO; ○, 804, 8.0% MeO.

Free Energy and BET Constants.—The free energy of water sorption at saturation is given by the equation

$$\Delta F = \frac{-RT}{M}\int_0^1 \frac{a\,dx}{x}$$

where a is the weight of water sorbed per 100 g. of dry sample, x is the relative aqueous vapor pressure, R the gas constant, T the absolute temperature, and M the molecular weight of water.[10,22] The values for ΔF_{25} in column three of Table III were obtained by multiplying the area under plots of a/x against x by RT/M. The values so found for the free energy are from 500 to 1000 cal./mole larger than for the proteins investigated by Bull.[10] Extrapolation of the a/x *versus* x curve to x equals one gives the amount of water, $(a_s)_{25}$, sorbed at saturation per 100 g. of sample. In column four of Table III, the values of $(a_s)_{25}$ are listed. These values are only approximate because of the difficulty of getting reliable moisture data at the relative humidity of 95% and the resulting uncertainty involved when the curve is extrapolated.

TABLE III

FREE ENERGY AND BET CONSTANTS CALCULATED FROM SORPTION AND DESORPTION MOISTURE ISOTHERMS

Sample		ΔF_{25} (cal./mole)	$(a_s)_{25}$	a_1	c
L51	Desorption	−1520	78	10.2	16.4
	Sorption			8.3	20.2
804	Desorption	−1620	72	9.1	11.4
L64	Desorption	−1630	76	10.3	16.2
	Sorption			9.5	9.1
L37P	Desorption	−1590	82	10.6	11.1
	Sorption			9.1	7.3
L81	Desorption	−1650	72	10.1	19.8
	Sorption			9.8	7.8
805	Desorption	−1680	72	10.5	15.8
L67	Desorption	−1700	84	10.6	18.9
	Sorption			9.5	19.2
619	Desorption	−1540	56	10.3	14.8
L69	Desorption	−1670	70	9.8	20.4
	Sorption			10.0	6.6

The saturation values, $(a_s)_{25}$, are quite large but appear to be reasonable in view of the high water contents observed at 95% relative humidity.

Stuewer[23] states that ultrafiltration experiments show that an apple pectin in aqueous solution was hydrated to the extent of about one-third of its weight. The values obtained by extrapolation from alcohol solutions indicated hydration to the extent of only about 25%. Both of these values are very much lower than those recorded in Table III.

The application of the adsorption theory of Brunauer, Emmett and Teller (BET)[24] to the observed moisture isotherms of the pectinic and pectic acids has been made in order that the results can be compared with similar analyses on other hydrophilic materials.[10,25]

Plots of $p/a(p_0 - p)$ as a function of x give reasonably straight lines for values of x between 0.15 and 0.45, where a is the grams of water sorbed per 100 g. of dry sample at water vapor pressure p, and p_0 is the water vapor pressure at saturation. The intercept on the ordinate is $1/a_1c$ and the slope is $(c - 1)/a_1c$, where c is approximately

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(22) G. E. Boyd and H. K. Livingston, THIS JOURNAL, **64**, 2383 (1942).

(23) R. F. Stuewer, *J. Phys. Chem.*, **42**, 305 (1938).

(24) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(25) L. Pauling, *ibid.*, **67**, 555 (1945); T. M. Shaw, *J. Chem. Physics*, **12**, 391 (1944).

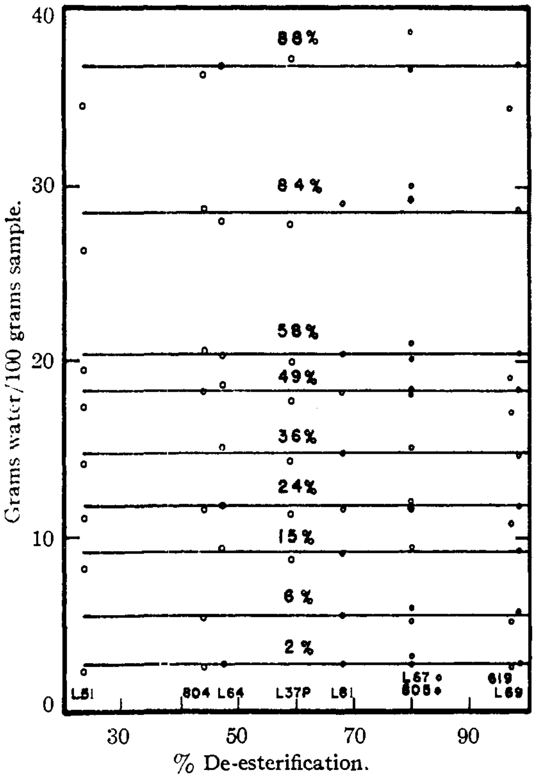

Fig. 6.—Variation of equilibrium moisture content (desorption) with per cent. de-esterification at the nine relative humidities shown on the curves.

equal to $e^{(E_1 - E_e)/RT}$. In the usual application of the BET theory to non-swelling sorbents, E_1 is taken as the heat of adsorption on the first layer, E_e the heat of liquefaction of the sorbate, and a_1 as the grams of sorbate necessary to cover the available surface in 100 grams of sorbent with a monolayer. The values of a_1 and c calculated from the BET plots are given in columns five and six of Table III, respectively.

It is interesting that the magnitude of a_1 is not only approximately constant for all the pectinic acids, but corresponds to about one water molecule per galacturonide unit. This amounts to one water molecule per three polar groups if equal weight is given to the hydroxyl, carboxyl, and esterified carboxyl groups.

X-Ray Spacings.—The X-ray spacing plotted in Figs. 3, 4 and 5 has been shown[12] to arise from planes which are parallel to the polygalacturonide chains. The variation in this spacing, therefore, reflects a change in interchain distance. The curves shown in Figs. 3, 4 and 5 give the variation of this reflection with water content at constant methoxyl content. The variation of this reflection with methoxyl content at constant moisture content can also be deduced from these curves.

It is interesting that when completely dry all but two samples have spacings that fall between 6.05 and 6.22 Å. This difference in spacing is approximately maintained for these same samples throughout the entire moisture range investigated. Of the two anomalous samples, L51 and 804, the pectinic acid sample L51 shows the most striking deviation. As shown in Fig. 3, the X-ray reflection does not appear to change appreciably with water content. This sample has a methoxyl content of 10.9% or about three methyl ester groups per four galacturonide units. The chains in this case evidently cannot coalesce when water is removed because of the prevalence of the methyl ester side chains. The diffuseness of the inner X-ray reflection obtained from L51 increases markedly with decrease in water content, indicating that a very irregular arrangement of the chains occurs when water is removed. At high relative humidities the X-ray reflection under discussion becomes much sharper, and in addition several new rings appear. It is apparent, therefore, that the chains assume a much more regular arrangement when hydrated than when dry. The reason why the interchain distance in L51 does not increase with increase in water content is not known, but may be due to the prevalence along the chain of the hydrophobic methyl groups.

The reason for the slightly different behavior of sample 804 as compared to the other samples may be due to the fact that this sample was acid de-esterified, while L64, which contains a comparable methyl ester content, was enzymatically de-esterified. It has been suggested[4b] that the acid treatment demethoxylates at random, while the enzyme removes the methyl ester groups continuously along the chain with which it is reacting. This results in a significantly different distribution of methyl ester groups after partial demethoxylation and may account for the observed difference in behavior between samples 804 and L64.

The X-ray spacing plotted in Figs. 3, 4 and 5 deviates in a significant way from the similar X-ray spacing of sodium pectate. In the case of sodium pectate, the analogous X-ray spacing increases with water content up to a water content of about 24% and then remains constant.[19] As shown in Figs. 3, 4 and 5, the crystallites in the pectinic and pectic acids, except L51, continue to sorb water throughout the entire range investigated. Swelling in the crystallites appears to be reaching a maximum value in some cases, notably 804, L64 and L67, but at a higher water content than 24%.

This difference in swelling behavior of the crystallites in the pectinic and pectic acids on the one hand, and sodium pectate on the other, is probably due to the higher degree of regularity which exists in the crystallites of sodium pectate as compared to those of the pectinic and pectic acids. The difference in crystallinity is readily apparent from a visual inspection of the X-ray photographs.

It is interesting that the two samples (sodium pectate and L51) in which the crystallites do not swell in the high moisture region are both water soluble, whereas the low methyl ester pectinic acids and pectic acid are not. Evidently the resistance to swelling at high relative humidities at 25° exhibited by the crystallites of sodium pectate and L51 is not related to the behavior of the sample when placed in contact with liquid water.

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Summary

The equilibrium moisture content at ten relative humidities between zero and 95% are given for seven pectinic and two pectic acids. The moisture content was found to be essentially independent of the methoxyl content.

The free energy change (average about 1600 cal./mole) is considerably higher than found for most proteins.

The BET constants have been calculated. The value of a_1 is nearly the same for all samples and corresponds to approximately one water molecule per galacturonic acid unit.

The variation of the equatorially accentuated X-ray reflection with water content has been determined. These results show that the interchain distance within the crystalline regions increases with increase in water content for all samples, except that having the highest methyl ester content (10.9%). In this latter sample the interchain separation appears to be independent of the water content.

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The Near Ultraviolet Absorption Spectra of the Vapors of the Monodeuterated Toluenes

BY A. R. CHOPPIN AND C. H. SMITH[1]

The study of the spectra of compounds in which hydrogen is partially or entirely replaced by deuterium is of importance in that it provides data on molecules having the same force constants but different masses and mass distributions. Such data are of assistance in identifying the vibrational forms corresponding to particular frequencies, and provide the additional frequencies which are often needed for the solution of secular equations and the calculation of numerical values for force constants.

Spectral data on deuterium substituted benzene derivatives are rather meager, although such data on benzene itself is extensive.[2,3,4,5] The infrared[6] and ultraviolet[7] absorption spectra of phenol-*d* and aniline-d_2 have been determined, but no report of work on benzene derivatives with nuclear deuteration has been found. This paper presents the results of a study of the near ultraviolet absorption spectra of the vapors of the following compounds: toluene, toluene-α-*d*, toluene-2-*d*, toluene-3-*d*, and toluene-4-*d*.[8] The spectrum of toluene vapor has been extensively investigated by many workers. The latest study is that of Ginsburg, Robertson and Matsen.[9] Such studies of the deuterated toluenes have not been reported.

Experimental

Preparation of Compounds.—Merck "Reagent Grade" toluene was purified by sulfonation, recrystallization of the sodium *p*-toluenesulfonate from saturated sodium chloride solution and regeneration of the toluene by steam distillation of a solution of the sodium *p*-toluenesulfonate in 80% sulfuric acid. The toluene layer was thoroughly washed with sodium hydroxide solution, cold concentrated sulfuric acid and with water. After drying over sodium and distilling over sodium, the middle fraction of the toluene boiled at 110.6 and had a refractive index (n^{20}_{D}) of 1.4965.

Each of the deuterated toluenes was prepared by treating the Grignard reagent, made from the appropriate halogenated toluene, with an equivalent amount of 99.9% deuterium oxide. Volatile components of the reaction mixture were removed by distillation, using an oil-bath. The temperature of the bath was not allowed to rise above 150°. The distillate was fractionated, using a packed eight-inch column, until the temperature of the vapors had risen to 50°. The distillate from the fractionation contained most of the ether and was discarded. The residue from the fractionation was thoroughly extracted with cold concentrated hydrochloric acid in order to remove the remainder of the ether. Then it was

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(1) Ethyl Corporation Research Fellow at Louisiana State University during this research.

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